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AD396995
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PORTON TECHNICAL PAPER No. 947

AN EXPERIMENTAL GAS CHROMATOGRAPHIC

C.W. AGENT DETECTION APPARATUS

FOR OVERALL SREGRADE CONDITIONS SEE INSIDE
COVER

BY

H. STRETCH

CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT
Porton Down, Salisbury, Wilts.

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AN EXPERIMENTAL GAS CHROMATOGRAPHIC C.W. AGENT DETECTION APPARATUS

by

H. STRETCH

SUMMARY

An experimental vapour detection apparatus has been devised consisting basically of a modified argon ionisation detector, the anode of which serves also as a built-in miniature gas-liquid chromatographic column.

Tests of the apparatus in the laboratory and in a gas chamber have shown that it is capable of detecting dangerous vapour concentrations of likely C.W. agents within a few seconds, even in the presence of innocuous vapours simulating likely atmospheric pollutants.

The reasons leading to the detector design are given and followed by a description of the modified anode and the operation of the detector. The causes of drift and sensitivity limitations are examined, and simple schemes to eliminate them are described. The report concludes with a description of the experimental C.W. agent detection apparatus, an account of the experiments undertaken, and the results obtained investigating characteristics such as the sensitivity, speed and linearity of response.

The results obtained are considered sufficiently encouraging to justify further investigation of the behaviour of an apparatus of this type in the natural atmosphere in a variety of environmental conditions, with emphasis on its possible development into a compact, automatic C.W. alarm for Service use.

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Physics Research Division.

(Sgd.) A.S.G. Hill,
Deputy Director.

PORTON TECHNICAL PAPER No. 947
Date: 7th March, 1966.
Copy No:

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INTRODUCTION

Attempts have been previously made to use gas chromatography in C.W. alarms. In the U.S.A. a number of instruments were made on conventional lines, each having a long heated column to separate the agent from air and innocuous pollutants, and either a flame or radioactive type of ionization detector (1). Development ceased once it was evident that a chromatograph alone could not be employed to identify agents.

The following paper gives preliminary details of a potential alarm system based on a modified argon detector (2), the modification consisting of the addition of a tiny column around the anode, separated by a 1-2.5 mm gap from the surrounding tritiated foil cathode (Fig. 1a). Vapours of high boiling substances present in air samples are isolated from low boiling pollutants by means of the column, and are subsequently measured and the amount related to the atmospheric concentration. High sensitivity is obtained by having the column inside the detector, where measurements are made before extensive dilution of the eluting vapour occurs, and also by taking a much larger sample than is possible in conventional chromatography. Other radioactive ionisation detectors can be similarly modified, thus enabling an electron capture detector for example, to be used to determine trace quantities of low vapour pressure halogen compounds in air.

Very little quantitative information exists about the atmospheric pollution caused by high boiling organic materials, because it occurs usually only at concentration levels far below those where C.W. agents produce rapidly harmful effects (3). For example, the amount of polynuclear hydrocarbons in the Pittsburgh atmosphere, stated to be $10^{-7} \mu g/l.$ (4), is too low to produce a false response in a C.W. alarm, and supports the belief that in general a process to separate innocuous high boiling substances from agents is unnecessary.

Design and development considerations

A conventional chromatographic analysis begins by injecting several milligrams of substance into a column, consisting of a long tube packed with inert particles previously coated with a thin film of involatile liquid. A steady flow of inert gas sweeps the vaporized substance through the column. Ideally each compound in the sample dissolves in the liquid coating, and is regenerated at a different rate, so each separately enters the detector at the end of the column, where a signal proportional to the instantaneous vapour concentration is produced. When the signals are recorded, a number of peaks corresponding to the amount of each compound is traced.

When analysis of the atmosphere is undertaken and the amount of material available in an air sample is very small, preconcentration is advantageous(5,6) but the time required is too long for use in an alarm. Only a small volume of air must be taken if the column is to operate in an efficient manner, and consequently a very sensitive detector is needed. An optimal sample volume for most columns is about 0.1 ml, but an air sample containing agent at 1 $\mu g/l.$ yields only 10^{-10}g of agent. Larger samples lead to a more gradual elution of all the components in the sample, and little separation is achieved.

Short columns of low plate number are necessary if rapid analysis is required and carrier gas supplies are to be conserved. Unfortunately with small columns, the resolution of adjacent peaks is poor, being proportional to plate number, as shown in the following equation (7)

$$R_{12} = \sqrt{N} \; \frac{(\alpha_{12} - 1)}{4 \, (1 + 1/K)}$$

Here R_{12} is the resolution, 'exact separation' occurring when $R_{12} = 1.5$; N is plate number, $_{12}$ is the 'solubility ratio' of the two substances in the liquid coating, and K the column capacity coefficient.

The time a substance is retained depends on the column temperature, peak width being in turn proportional to retention time as shown in the following equation (8)

$$N = 8 \left(\frac{t_r f}{B_e} \right)^2$$

where t_r is retention time, f flow rate and B_e peak width at height h/e. Consequently substances of low volatility are retained for comparatively long periods in unheated columns, only gradually eluting. Sharper peaks are obtained when the column temperature is raised to within a few degrees of the boiling point of each component in the sample, which is impossible with unknown substances. No advantage is gained by having a column at a temperature still some way from the boiling point; this became clear when V agent simulants were injected in small amounts into a $\frac{1}{2}$ inch long column heated to $150^{\circ}C$. Although the column was in the entrance to the ion chamber of the detector, simulant vapours could not be detected. Failure may have been due either to excessive dilution of regenerated vapours prior to detection or to inefficient mixing of relatively large vapour molecules with metastable argon, which spends the whole of its existence near to the cathode surface (9). Both effects can be reduced by having the column inside the detector, and if in addition a larger sample is taken (at the expense of column efficiency) simulant vapours are easily detected.

Experimental work was undertaken to find out if adequate separations could be obtained. In the following sections the modified detector and ancillary equipment are described, and the results of tests designed to measure the sensitivity to agents and to normal pollutants are recorded.

As is often the case in projects of this type, the work progressed more by way of a series of "ad hoc" experiments designed to establish specific facts or evaluate minor design changes, than along the lines of a systematic research investigation, and this should be borne in mind in reading this report.

APPARATUS

The apparatus consists of (i) detector, (ii) magnetic relay allowing air and argon to flow alternately through the detector, (iii) d.c. amplifier to magnify the detector output, (iv) E.H.T. supply to the detector, (v) thermostatic control and associated heater, (vi) small pump to draw air through the detector and (vii) argon cylinder fitted with a fine control. The unmodified detector is described in a previous paper (2) and the modifications and subsequent effects on the performance are discussed in the following section. The remainder of the apparatus is described in Appendix 2.

The detector anode

A small cylinder made from 200 B.S.S. brass gauze was arranged coaxially around the brass rod employed as anode, and soldered to it. One end of the cylinder rested on an end plate of the ion chamber, and the other was 2 mm away from the opposite end plate. The space between the cylinder and rod was filled with glass wool and the complete anode assembly coated with a film of liquid partitioner by dipping into a 1% solution in acetone and subsequently drying at 130°C. A cross section of a detector is shown in Fig. 1a.

The detector sensitivity was determined experimentally by measuring the response to several vapours, approximately in the first place by holding a plug of cotton wool soaked in the appropriate liquid near to the entrance tube, and later by sampling known vapour concentrations in a 100 m^3 chamber.

Cylinders of different diameter were fitted in turn into the anode assembly and tested, and it was found that as the distance between anode and cathode was increased, a proportionately higher anode voltage was required to maintain optimum sensitivity. For example, highest sensitivity occurred at

900V when an 8 mm diameter cylinder was employed, and at 1400 volts when the cylinder was 6 mm diameter, in both cases the field strength being near to the stipulated value. However arcing occurred on several occasions when detectors fitted with the larger size of cylinder were used over an extended period, whereas those fitted with a 6mm diameter cylinder have shown no tendency to arc. As far as can be ascertained from the results of the few tests which have been undertaken, a similar sensitivity can be obtained with all detectors fitted with cylinders of between 6 and 8.5 mm diameter, and consequently a 6 mm size cylinder is preferred at the present.

Detector standing current

The following operating conditions were used:-

Anode cylinder diameter 7 mm   Anode voltage 1200V

Argon flow 150 ml/min   Partitioner equal parts Carbowax

20M and dinonyl phthalate.

Since a potential difference of 0.8V was measured across the grid of the first amplifier through a total of $32\Omega M$, the detector standing current was 2.5×10^{-8} A. The corresponding figure quoted for a miniature coaxial detector possessing a solid brass cylindrical anode operated at 300V was stated to be 6.1×10^{-9} A when 50 ml/min flow of argon was employed (10). It appears therefore that no significant increase in standing current is caused by the presence of liquid partitioner in the ion chamber.

OPERATION

Fig. 1b is a block diagram showing the equipment required to detect rapidly the vapours of high boiling substances in the atmosphere. Details of the separate items are given in the Appendix. In the apparatus the changes in detector current resulting from the presence of ionised organic vapours, produce a corresponding change in readings on a microammeter connected in the amplifier output.

Tests were conducted as follows; after the apparatus had been switched on and air and argon were flowing alternately through the ion chamber, the meter was set to a suitable reading in an interval when argon was flowing. A zero reading was indicated in the subsequent period of air flow, but on reintroducing argon a rapid increase occurred nearly to the set figure. During the remaining time argon was flowing, a slight but steady fall in meter reading was noted. The output signals could be regarded as trapezoidal pulses of identical shape, width t seconds (argon flow time) and height h, the maximum reading, thus allowing a reading, corresponding to maximum concentration from each sample, to be determined simply by subtracting h_0, the signal in clean air, from that in air containing vapour, h_v.

Stability

Drift appeared to be due essentially to three causes:-

(1) **Changing detector temperature.** The magnitude of this effect was measured by placing an ionization detector in an insulated box containing a small heater which could be thermostatically controlled. The temperature of the box was raised in a series of $0.5^{\circ}C$ intervals, in which the detector was allowed to attain equilibrium. Microammeter readings were taken at each temperature and a graph constructed. The slope of the straight line produced indicated that output current increased by $12\mu A$ with each $1^{\circ}C$ rise in temperature.

(2) **Fluctuations in argon flow rate.** The size of this effect when using the same detector was obtained graphically from the following figures.

Table 1

The effect of change in argon flow rate on output meter readings

Flow rate	Output current
ml/min	μA
140	10
120	50
95	100
70	150
45	200

They show that an increase of 1ml/min in the argon flow rate depressed the output current by $2 \mu A$.

(3) <u>Air sample pressure and temperature changes.</u> Microammeter readings
were taken during the aspiration of test vapours from a 100m^3 chamber,
inside which detection apparatus was operated. The extractor slightly lowered
the pressure in the chamber, and consequently that in the detector ion chamber,
also. This led to enhanced current readings at first. However, as fresh
cold air entered the chamber and was sampled, it apparently lowered the
temperature inside the detector, decreasing the standing current to a new low
value. Consequently tests were undertaken only after the detector had reached
a temperature equilibrium.

Variations in atmospheric temperature and pressure would undoubtedly lead
to some drift if the apparatus were employed under Service conditions, but it
is believed that over short intervals of time this will be insignificant
compared with the response produced by rapidly effective agent concentrations.
However, if in practice the drift is found to interfere with agent recognition,
a slightly more complicated sampling procedure could be adopted to overcome
this difficulty.

Suitably simple measures were adopted to overcome drift in the experi-
mental detection apparatus and these are incorporated in the instrument
described in the appendix. A similar instrument having a sensitivity of
$24\mu A/\mu g/l.$ to dimethylaniline vapour showed a drift of only $30\mu A$ over 16 hours
in a laboratory, and this was almost wholly in a negative direction due to
overnight cooling, and substantially free from rapid fluctuations. It
appeared to be due to insufficient thermostatic control.

VAPOUR SAMPLING

Experimental details and results of tests, all of which were obtained
with a modified anode coated with Apiezon grease and dinonyl phthalate, are
given in Appendix 1.

Table 2 and Figs. 4a and 4b show that a marked increase in signal was
measured when the sampling time was changed from 1 to 2 seconds. This
occurred when air samples containing either the vapours of the high boiling
substance dimethylaniline, or hexane, used to simulate a common atmospheric

pollutant, were sampled. Additional small gains were made by using still longer sampling times, until a maximum response of $24\mu A$ from a dimethylaniline nominal concentration of $1\mu g/1$. was obtained from a sample collected over 6 seconds. Using a sampling time of 6 seconds, a number of tests were undertaken, each at a different sampling rate, and the results are shown in Table 3 and Figs. 4a and 4c. A steady sharp increase in signal was measured up to a flow rate of 500 ml/min, but this was followed by a slight decrease at 2 litre/min. It was concluded that a sample of 50 ml or more sampled at 500 ml/min produced the best results, although in practice the somewhat lower sensitivity obtained from 50 ml. air sampled in 2 to 3 seconds may be acceptable. When optimum sampling was employed, the signal produced by a $1\mu g/1$ dimethylaniline concentration was about fifty times that given by the same hexane concentration.

Sensitivity was unaffected by changes in argon flow for flow rates ranging from 50 to 150 ml/min, the only effect being to change the time required to reach maximum reading from 6 seconds at 50 ml/min to 3.5 seconds at the higher rate.

The results of tests undertaken to find the linearity of response are given in Table 4 and Figs 4d, 4e and 4f. They show that the response to either hexane or xylene remained linear even when relatively high concentrations were sampled. Non-linearity was found with low concentrations of dimethylaniline, which may have resulted from the use of an unsuitable partitioner. The response with the other partitioners will be tested.

The time required to obtain maximum response from a vapour concentration was next investigated and the results obtained are given in Table 5. First the air signal inside the chamber was measured. A glass tube was employed to sample air outside the chamber, and a small difference between inside and outside measurements was subsequently used to correct sample readings. While outside air was being sampled, the test material was volatilised, and after allowing 4 minutes for the establishment of a uniform vapour distribution a person inside the chamber disconnected the

glass tube. Signals were recorded at intervals until a maximum reading was obtained. The tube was then replaced and the time to attain background signal was noted. With both dimethylaniline and triethyl phosphate concentrations a very rapid rise in signal strength was observed and both were equally rapidly expelled from the detector. The same quick build up followed by speedy removal was found when substances of very low volatility, such as diethyl phthalate, were sampled from aspirators.

Table 6 shows the results of tests investigating the effect of the electric field across the detector ion chamber. Over the voltage range examined, the increase in signal was proportional to the applied EHT.

Finally tests have been made on vapour concentrations of a wide variety of substances. Where it has proved possible to obtain uniform dispersal, low concentrations of all the high boiling substances tested have been measured at a sensitivity of $20-30\mu A/\mu g/l.$, whereas a lower range of sensitivities has been recorded with more volatile substances. So far the best results obtained using a GB concentration have indicated a sensitivity of $10\mu A/\mu g/l.$ It may be possible to increase this figure by judiciously choosing the liquid partioner. No significant difference in response between fairly dry air and air of relative humidity approaching saturation has been detected.

CONCLUSIONS AND RECOMMENDATIONS

An experimental apparatus employing a miniature coaxial argon ionization detector having the anode modified to operate as a built-in separating column, has been constructed and appears to be capable of detecting vapour concentrations of likely C.W. agents within a few seconds, even in the presence of innocuous vapours simulating likely atmospheric pollutants. The results of tests conducted in the laboratory and in a $100m^3$ chamber are sufficiently encouraging to justify further investigation of the behaviour of an apparatus of this type in the natural atmosphere in a variety of environmental conditions, with emphasis on its possible development into a compact, portable automatic C.W. alarm for Service use. The response of the apparatus to C.W. agents in aerosol form should also be examined.

Until a prototype field instrument has been constructed with careful attention to all factors affecting sensitivity and stability, the true potential of the device cannot be assessed.

ACKNOWLEDGEMENTS

Mr. R. Henville helped to construct the experimental detection apparatus and assisted in the trials. Mr. A. R. Burbage advised on the electronics.

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Table 2

The effect of sample time on the sensitivity

Air flow 500 ml/min
Argon flow 120 ml/min

Column coating Apiezon grease and
dinonyl phthalate

Substance	Nominal concentration $\mu g/l.$	Sample time in seconds	Sample volume in ml	Reading in μA	Sensi-tivity $\mu A/\mu g/l.$	Ratio of DMA response to hexane response
Dimethyl-aniline	2	1	8.3	30	15	15
"	2	2	16.6	40	20	
"	2	4	33.3	43	21.5	
"	2	6	50	48	24	48
"	2	10	83.3	49	24.5	24.5
Hexane	20.5	1		8	0.4	
"	20.5	6		11	0.5	
"	20.5	10		20	1	

All DMA results were obtained in one day and hexane results the next day.

Table 2a

Flow rate 2000 ml/min, otherwise similar conditions to those above

Dimethyl-aniline	2	2	67	30	15	
	2	4	134	34	17	
	2	6	200	40	20	
	2	10	333	40	20	

Table 3

The effect of changing the sample flow rate

Sample flow time 6 seconds

Substance	Sample flow rate ml/min	Sample volume in ml	Sensitivity $\mu A/\mu g/l.$
Dimethyl-aniline	20	2	12
"	50	5	14
"	100	10	16
"	300	30	18
"	500	50	24
"	2000	200	20

Table 4

Linearity of response

Apieson-dinonyl
phthalate coating

Substance	Nominal concentration $\mu g/l.$	Reading μA	Sensitivity $\mu A/\mu g/l.$
Hexane	3.4	1.5	0.44
	6.8	6	0.88
	10.2	8.5	0.84
	13.6	12	0.88
	16.9	16	0.95
	20.4	19.5	0.95
	27.2	26	0.95
	34	32	0.94
Xylene	1.8	8	4.4
	3.5	12	3.4
	5.3	23	4.3
	15.9	54	3.4
	21.2	72	3.4
Dimethyl aniline	1	19	19
	2	31	15.5
	3	43	14.5
	4	53	13.3
	6	63	10.5
	7	66	9.4
	10	75	7.5

In the experiments leading to the results given in the above table, the substance was volatilised and the apparatus allowed to attain a maximum response. Then the concentration was reinforced with more of the substance, and readings were taken again until a maximum value was recorded.

Table 5

Speed of response

(1) Dimethylaniline 1.5µg/l.

Time in seconds	Reading µA	Sensitivity µA/µg/l.	
0	0		sampling commenced
4	4	3	
16	14	9	
28	19	13	
40	27	18	maximum
0	27		clean air sampled
24	18	12	
36	13	8	
48	4	3	
60	0		

(2) Triethyl phosphate at a nominal concentration of 3µg/l.

0	0		sampling commenced
16	30	10	
40	33	11	

With successive samples a series of slight rises was recorded up
to a maximum reading of 35.

0	35		clean air sampled
24	15	5	
48	5	2	
60	0		

Table 6

The effect of changing EHT

Vapour was sampled from a 5l. aspirator containing diethyl phthalate (a description is given in the section dealing with apparatus).

Voltage	Reading μA	Detector sensitivity μA/μg/l.	Reading increase μA	dR/dV
1250	64	13.9	0	
1300	82	17.8	18	0.36
1350	100	21.6	36	0.36
1400	116	24.7	52	0.36
1450	136	29.5	72	0.36

A vapour concentration of 4.6 g/l. was used to calculate sensitivities

AUXILIARY APPARATUS

(i) The magnetic relay valve

A 3 port micro electric valve (Martonair Ltd., type S557CZ/1) supplied with $\frac{1}{8}$ B.S.P. ports was used. One inlet was connected to a supply of dried argon and the other through an orifice to a small electric pump. The outlet was connected to the detector. Normally argon flowed through the valve and into the detector, but on energizing the relay with 12V, 1A a.c. or d.c., the argon flow was stopped and instead air was drawn through the detector. In early experiments the respective flow times were controlled by a pair of process timers (Airmec Ltd.), but these were later replaced by a switch operated every 6 seconds by means of a transistorized multi-vibrator oscillator (Fig. 2a).

A pair of sample valves was tested in a tandem arrangement allowing uninterrupted flow of the air and argon. The stability of the signal was unchanged, so this theoretically sound but complicated system was abandoned.

(ii) The d.c. amplifier

A differential amplifier of 120MΩ input resistance, gain 5 - 10,000 was required. A circuit diagram of a mains operated amplifier which was employed is shown in Fig. 2b. A standing voltage of about 3V appeared across the input when the amplifier was in use in the detector.

Three alternative arrangements will be tried for a portable amplifier. The first will use valves in cascade, H.T. being supplied from a transistor convertor; this will be bulky but there should be no particular difficulty in meeting the input and drift requirements. The second will employ field effect transistors, which alone amongst transistors have the necessary input characteristics, and the third will be a hybrid of the two previous systems.

(iii) Thermostat

A $4\frac{1}{2}$ inch cube box contained the detector and a small heater wound with a few inches of $27\Omega/ft$ resistance wire; 0.3A at 12V was required to operate the heater. A thermometer type of thermistor (Mullard VA3700 series) was inserted through a hole in the top of the box, and adjusted until the tip almost touched the detector. It was used in combination with a sensitive amplifier (11) to keep the box temperature at $40^{\circ} \pm 0.02^{\circ}C$. This detector box was fitted into one corner of a 12 inch cube Perspex box, which also contained the magnetic relay, timer and d.c. amplifier. The heat dissipated by the amplifier helped in maintaining the detector at the required temperature.

(iv) The argon supply

A fine control needle valve (Edwards 'Speedivac' Model LB) was necessary to ensure a constant flow rate.

The water content of the gas used was specified as <8 p.p.m. There is evidence (12) that a gain in sensitivity might be achieved by reducing this water content. Argon can be dried to 6 p.p.m. by means of anhydrous magnesium perchlorate, but when short tubes packed with this substance were connected in the argon line, no increase in sensitivity was measured. It was clear that more sophisticated and complicated procedures were necessary to produce a significant improvement, and these would be unsuitable in a portable instrument. Accordingly no further attempts were made to dry the argon.

Sampling techniques

(a) Inside the $100m^3$ chamber

The apparatus was placed inside the chamber and the amplifier output connected by long leads to a $100\mu A$ meter on the outside. Both argon and sample flow rates were measured and adjusted when necessary, then sampling was commenced, and the microammeter readings recorded. After a time readings became constant, and the value was recorded as the 'clean air' reading. An
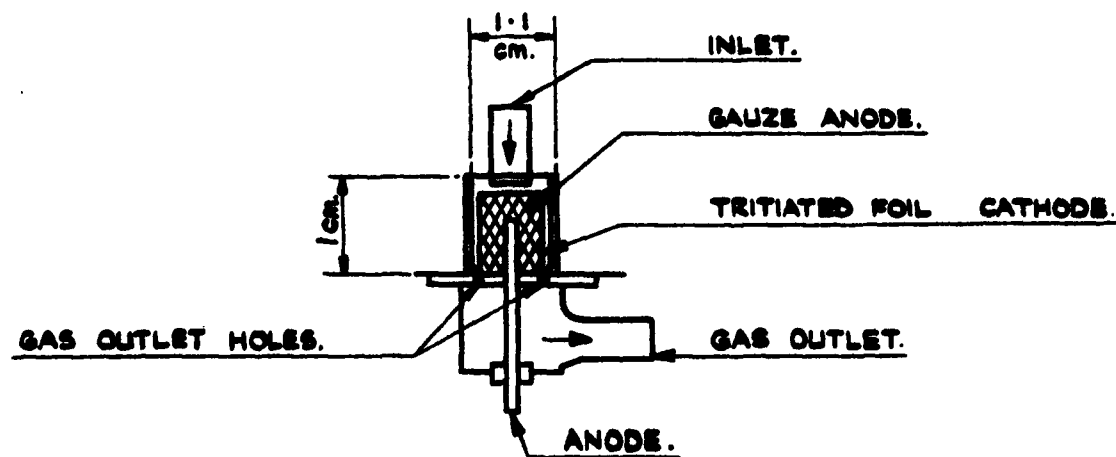
appropriate amount of test liquid to give a nominal vapour concentration
was weighed into a bottle and evaporated on a hot plate inside the chamber,
as soon as the "clean air" reading was obtained. Several mixing fans were
employed to produce a uniform concentration. Readings were taken through-
out this mixing period; they increased to a maximum value in about 3 to
4 minutes, then slowly decreased as vapour sorbed on the chamber walls.
Unfortunately when substances of very low volatility were tested, the
signal amplitude was found to be dependent on the sampling position, so
the following procedure was adopted.

(b) Reference source

The following procedure was also used to produce a reference source
when polluted atmospheres were examined.

Two 51. aspirators were connected by a 2-way tap to the entrance of
the detector. One was left open at the top to the air, but the other was
sealed with a bung supporting an agitator. 100ml of the test liquid was
stirred for 30 minutes, then vapour samples were taken through the exit
hole 1 inch above the liquid surface. A plug of cotton wool in the exit
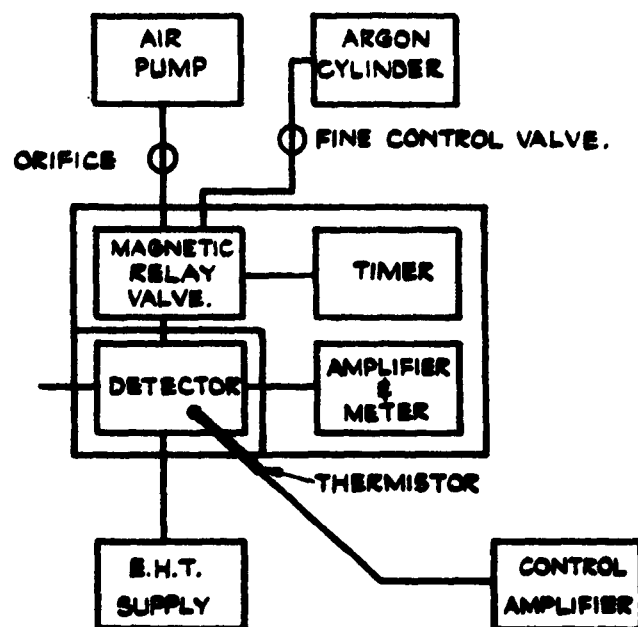prevented any aerosol reaching the detector.

GAS CHROMATOGRAPHIC DETECTOR.

FIG. 1a

PORTON TECHNICAL PAPER 947

P 3415

AIR PUMP

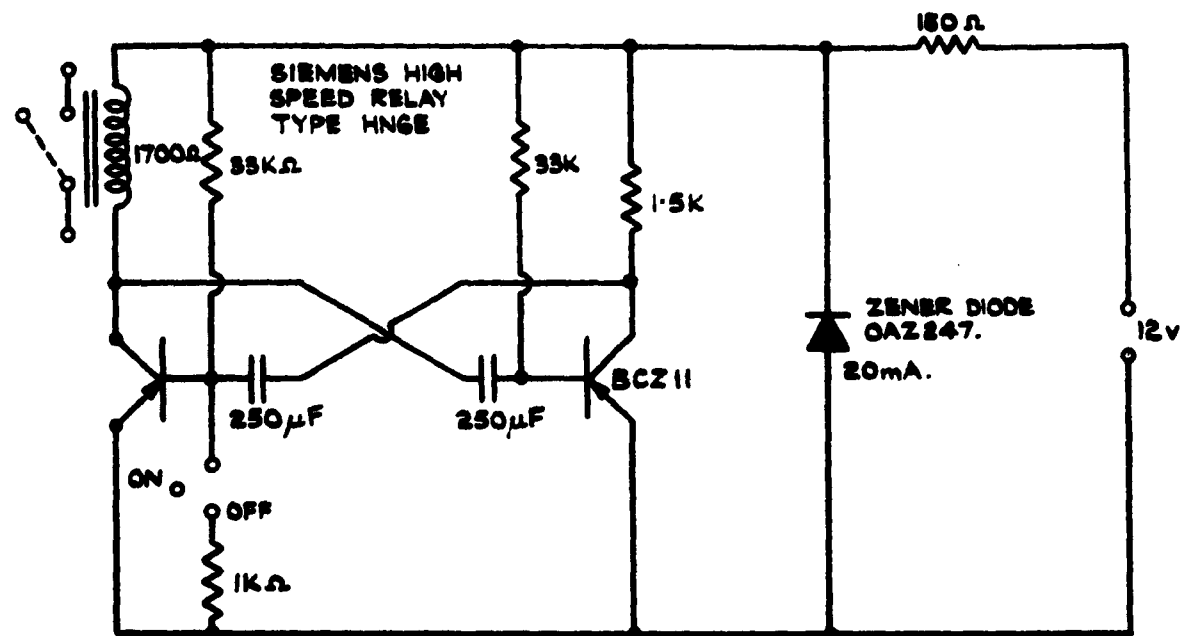ARGON CYLINDER

ORIFICE FINE CONTROL VALVE.

MAGNETIC RELAY VALVE.

TIMER

DETECTOR

AMPLIFIER & METER

THERMISTOR

E.H.T. SUPPLY

CONTROL AMPLIFIER

BLOCK DIAGRAM OF EXPERIMENTAL GAS
CHROMATOGRAPHIC DETECTION APPARATUS.

FIG.1b

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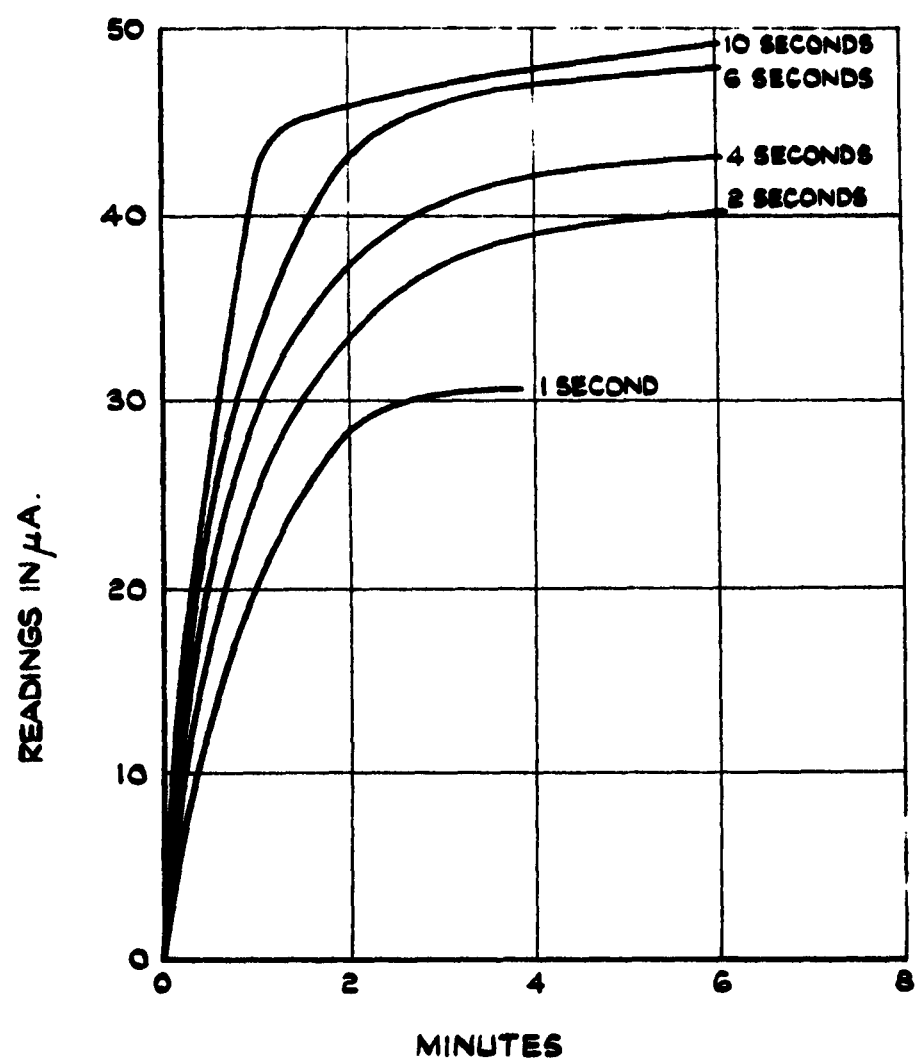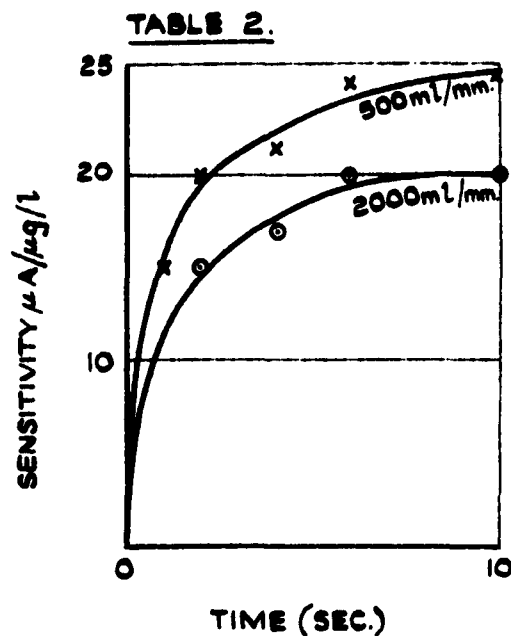P 3416

TIMER.

FIG. 2a

P 3417

FIG. 2b

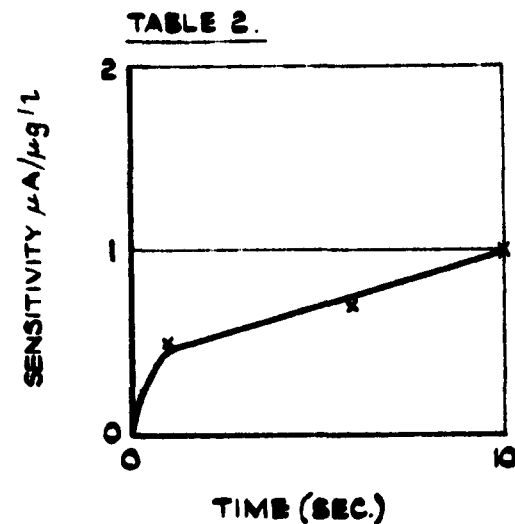d.c. AMPLIFIER.

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THE EFFECT OF CHANGING SAMPLING TIME.

FIG. 3
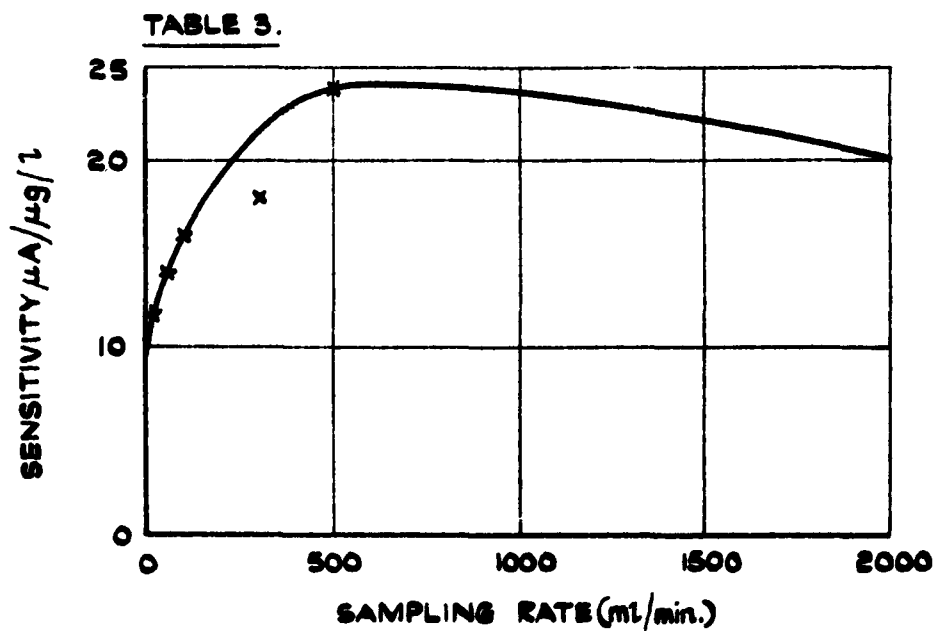
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TABLE 2.

(a) DIMETHYLANILINE

TABLE 2.

(b) HEXANE.

THE EFFECT OF SAMPLING TIME ON SENSITIVITY.

TABLE 3.

(c) DIMETHYLANILINE.

THE EFFECT OF SAMPLING RATE ON SENSITIVITY.

FIG. 4 (a) (b) (c)

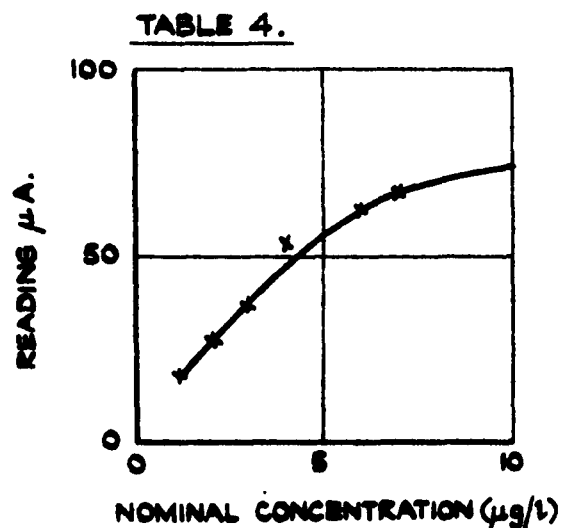PORTON TECHNICAL PAPER 947

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TABLE 4.

(d) HEXANE.

TABLE 4.
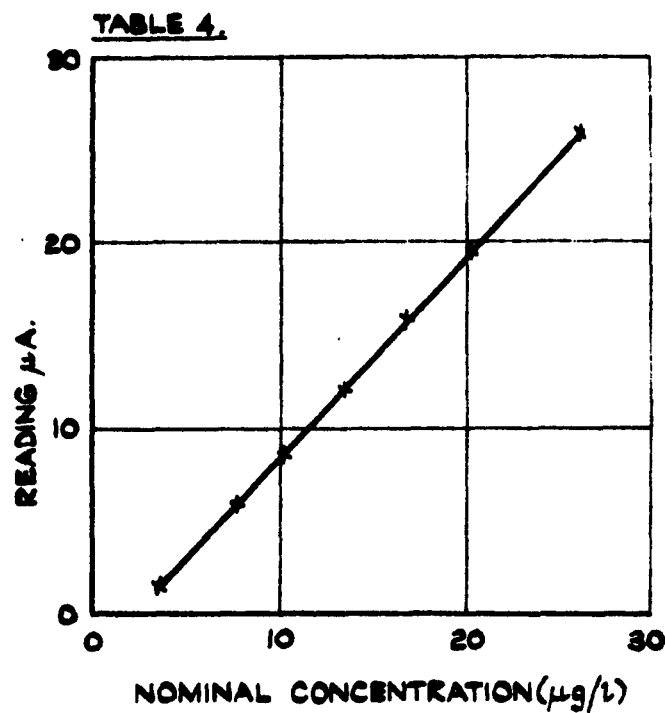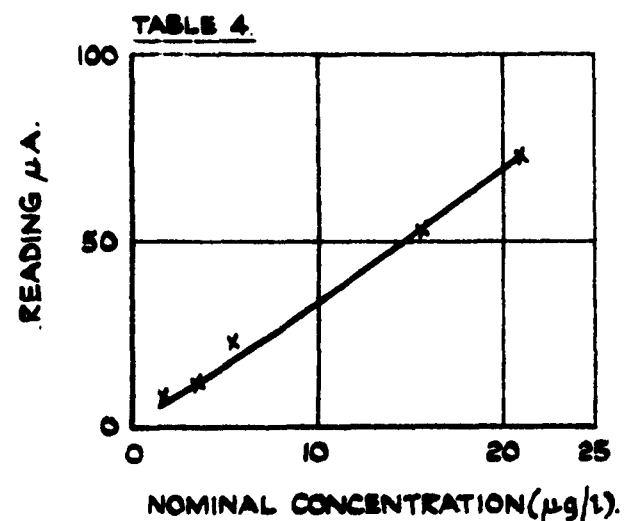
(e) XYLENE

THE LINEARITY OF RESPONSE.

TABLE 4.

(f) DIMETHYLANILINE

THE LINEARITY OF RESPONSE.

FIG. 4 (d)(e)(f)

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